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RESEARCH MEMORANDUM

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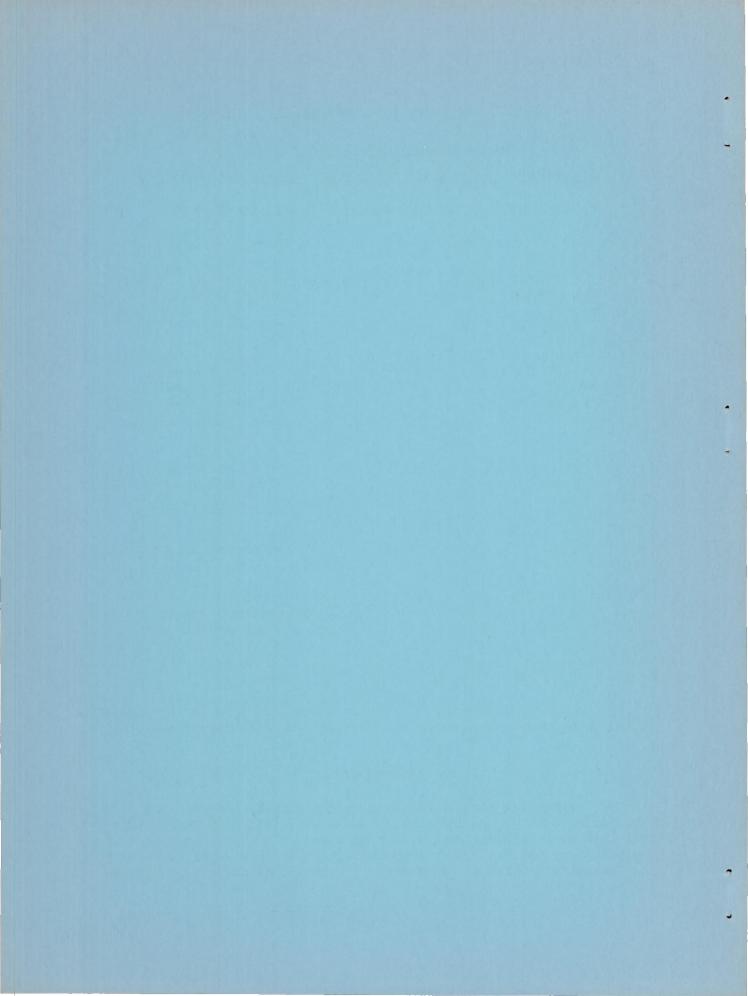
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NATIONAL ADVISORY COMMITTEE
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PRELIMINARY INVESTIGATION OF A CHEMICAL STARTING TECHNIQUE

FOR THE ACID - GASOLINE ROCKET PROPELLANT SYSTEM

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SUMMARY

A preliminary investigation of the use of a small quantity of fluid that ignites spontaneously with nitric acid to initiate the acid - gasoline reaction was carried out in a 200-pound-thrust uncooled engine with a characteristic length of 30 inches at temperatures ranging from 50° to -85° F. For convenience of experimentation, the starting process was divided into two phases: ignition, the result of reaction between the igniter fluid and the acid; and transition, the replacement of igniter fluid by gasoline to give steady-state combustion.

It was found that ignition could be obtained at -85° F with fuel blends of aromatic amines and triethylamine with red fuming nitric acid (RFNA) containing approximately 19 percent nitrogen dioxide and 3 to 5 percent water used as an oxidant. For the engine configuration employed, the maximum initial flow rate of propellants which would permit ignition to occur decreased as temperature was decreased; that is, a decrease in valve opening rate was required.

With the transition flow program used, transition to gasoline was possible at 40° F with all igniter fluids tried; whereas at -40° F, transition could be obtained only with hydrazine hydrate containing a small quantity of gasoline in suspension. As reactivity of the main fuel was increased by substituting triethylamine for gasoline, transition was obtained at -85° F with the particular flow program used.

The tendency of several igniter fluids to form tars in the combustion chamber decreased as the aromatic content of the fluid was decreased.

INTRODUCTION

For large-scale use and moderate flight ranges, the gasoline - nitric-acid rocket propellant system appears logistically attractive since both materials are available from numerous sources and in quantities which are unlimited when compared with available supplies of many other rocket propellants. Furthermore, gasoline is already so widely

used for aircraft propulsion that the additional quantities required for
rocket-engine operations would demand little or no expansion of present
distribution channels. Methods for distributing nitric acid in tonnage
quantities are also well established.

Before this propellant system can become entirely satisfactory for
field use, several problems must be solved. One such problem is to
obtain reliable starting at low ambient temperatures. The problem is
especially severe for assisted-take-off units operating under arctic
conditions and in units designed for additional thrust at high altitude
in fighter aircraft or long-range bombers when repeated starts without
intermediate servicing are required.

Two basic methods appear feasible for igniting the gasoline - acid
system, namely, the use of electrical igniters or of chemical igniters.
Studies of spark ignition in hydrocarbon-air mixtures (refs. 1 and 2)
have shown that, as temperature and pressure are decreased, the required
electrical energy is increased; it is also known (refs. 3 to 6) that, as
temperature is decreased, the ignition lag of spontaneously igniting
propellants increases. It would therefore be expected that, as ambient
temperature is decreased, the gasoline - acid system becomes more diffi-
cult to ignite.

The investigation reported herein was concerned with the chemical
starting method and, in particular, with the use of an igniter fluid
which precedes the gasoline into the combustion chamber and ignites
spontaneously with the acid; the heat of reaction serves to ignite the
gasoline which follows. For ease of analysis and experimentation, the
starting process has been divided into two phases. The first phase,
called ignition, is the reaction between igniter fuel and acid. The
second phase, called transition, is the replacement of igniter fuel by
running fuel until steady-state combustion is attained. Completion of
both phases is called a start.

The purpose of the investigation, presented herein and conducted at
the NACA Lewis laboratory, was to determine the rocket-engine ignition
characteristics of several fuels that gave low ignition lags with acid
in bench apparatus, to determine some of the fluid flow factors governing
transition between igniter fuel and running fuel, and to determine the
coking tendencies of several types of igniter fuel.

The technique used was to cool the 200-pound-thrust engine and
propellants to a desired temperature, adjust the valve opening rate, and
measure the success of ignition or transition by a time record of
combustion-chamber pressure. The primary variables were temperature,
valve opening time, igniter fluid, and method of blending starting and
running fuel.

APPARATUS

The apparatus consisted of a thrust cylinder with an impinging-jet injector, a hydraulically actuated propellant valve, a combined blending device and tank for igniter fuel, tanks for running fuel and oxidant, and a refrigeration system.

Thrust cylinder. - The thrust cylinder was uncooled and had a nominal thrust rating of 200 pounds, a characteristic length (ratio of chamber volume to nozzle-throat area) of approximately 30 inches, and a design operating pressure of 450 pounds per square inch gage. The injector was of the impinging-jet type with four sets of holes spaced 90° apart. Each set consisted of two acid holes and one fuel hole, with fuel on the inside. Details of the thrust cylinder are shown in figure 1.

Propellant valve. - The propellant valve was a modified version of that described in reference 7 and permitted an acid lead into the combustion chamber. The fuel and acid valve pintles were connected by a yoke which was actuated hydraulically; the valve opening rate was adjusted by changing restrictor orifices and hydraulic pressure.

Flow characteristics of the propellant valve-injector combination are shown in figure 2. The flow rates are based on a propellant supply pressure of 550 pounds per square inch gage and atmospheric pressure in the chamber. This condition approximates that in the rocket engine prior to ignition. The flow coefficients used to calculate the curves were obtained by calibrations with water-glycerine mixtures over a range of Reynolds numbers.

Igniter fuel and transition cylinder. - Transition from igniter fuel to running fuel was controlled by a piston and cylinder device which served the dual purposes of containing the igniter fuel as well as controlling the transition from igniter fuel to running fuel. Figure 3 is a schematic drawing of the entire propellant system as well as the details of the flow control cylinder.

The flow control cylinder functions in the following manner: The desired quantity of igniter fuel is loaded into the cylinder forcing the piston to the rear. Running fuel is loaded into its tank and air is bled from the system by means of hand valves. When the main fuel tank is pressurized and the propellant valve opened, pure igniter fuel enters the thrust chamber until the piston begins to uncover the ports in the side of the cylinder. At this time running fuel is mixed with igniter fuel. When the piston reaches the extreme forward position, pure running fuel is entering the thrust cylinder. By using high-speed motion pictures and colored water it was determined that the volume of blended igniter fuel and starting fuel was approximately $1\frac{3}{4}$ cubic inches. Total volume of the igniter-fuel cylinder was 15 cubic inches.

Refrigeration system. - For cold runs the entire rocket assembly, including thrust cylinder, valves, and tanks, was submerged in a tank filled with methylene chloride. Constant temperature was maintained by circulating the methylene chloride through a system consisting of a warm bath (water) and a cold bath (dry ice and alcohol), mixing valves, and a controller, as shown schematically in figure 4.

For warm runs the container was filled with water to help maintain constant temperature and to help minimize explosion damage.

Instrumentation. - Recording bourdon-tube-type pressure gages were used to measure fuel and oxidant supply pressures, injection pressures, and combustion-chamber pressure. These instruments had an accuracy of ±2 percent of full scale, which in most cases was ±15 pounds per square inch. The propellant valve position was converted to electrical voltage by means of a rack and pinion operating a variable resistance and was continuously recorded by means of a recording potentiometer.

Temperatures were measured by two thermocouples in each propellant tank, one thermocouple in each propellant line, and two thermocouples in the coolant bath.

PROCEDURE

For ignition runs, the igniter fuel was loaded into the fuel control cylinder and the running-fuel tank was left empty. Direct gas pressure on the piston forced igniter fuel into the engine. For transition runs, both igniter fuel and running fuel were loaded into the appropriate tanks. In all cases, enough acid was loaded to provide an over-all oxidant-to-fuel weight ratio of four plus acid lead and acid override.

After loading propellants, refrigerant was admitted to the coolant bath and sufficient time allowed for all thermocouples to reach the same temperature within 1° or 2°. At this point the engine was pressurized and fired.

Satisfactory ignition was adjudged by sound and a continuously rising chamber pressure trace consistent with valve opening rate. Starting was considered satisfactory when the pressure trace leveled off at design chamber pressure.

The fuels used consisted of gasoline (MIL-F-5572, 115/145); triethylamine; turpentine; toluene; diallyl sulfide; mixed alkyl thiophosphites; 70 percent triethylamine, 30 percent orthotoluidine; 50 percent triethylamine, 50 percent diallylaniline; 50 percent triethylamine, 50 percent diallylamine; hydrazine hydrate (64 percent hydrazine); hydrazine hydrate plus 5 percent suspended gasoline; and 63 percent

triethylamine, 27 percent orthotoluidine, 10 percent gasoline. All
materials used were of commercial grade and blended on a volume basis at
70° F. The suspension of gasoline in hydrazine hydrate was temporarily
stabilized by small amounts of stearic and oleic acids.

The acids were blended on a weight basis and the assays are shown
in the following table:

Oxidant	Composition by weight		
	HNO_3	NO_2	H_2O
[a]WFNA	97.5	0.6	1.9
RFNA 1	77.7-76.6	18.7-19.6	3.6-3.8
RFNA 2	76.0	18.4	5.6

[a]White fuming nitric acid

RESULTS AND DISCUSSION

Ignition temperature limits. - In references 3 and 4, a 50:50 blend
of triethylamine and diallylaniline, and a 70:30 blend of triethylamine
and orthotoluidine are reported to have ignition delays at -87° F of 50
and 62 milliseconds, respectively, with acids containing 3 to 5 percent
water and 16 to 19 percent nitrogen dioxide. In this investigation it was
found that those fuels ignited in a satisfactory manner in the engine at
-85° F with red fuming nitric acid containing approximately 16 to 19 per-
cent nitrogen dioxide and 3 to 5 percent water. These results tend to
confirm the opinion expressed in the references that these fuels are
satisfactory for use at least as low as -76° F, the lower specification
temperature for military equipment.

Effect of temperature on allowable igniter fuel flow. - The minimum
valve opening times which would permit ignition of the 70:30 blend of
triethylamine - orthotoluidine with two compositions of red fuming nitric
acid are shown in figure 5 as functions of initial ambient temperature.
In general, the allowable time increased from less than 0.1 second at
50° F to from 2 to 4.5 seconds at -85° F. The higher of the two values
at -85° F can be accounted for, in part, by the longer ignition lag of
the acid containing 5 percent water as compared with the acid containing
3 percent water. Figure 6 shows the calculated propellant flows corre-
sponding to the valve opening times at 50° and -85° F, and figure 7
compares the ignition lag curve obtained in bench-scale apparatus
(ref. 4) with the minimum-valve-opening-time curve.

Two general conclusions can be obtained from these data:

(1) As the temperature is decreased, the valve opening time required for ignition increased, and from the calibration curves (fig. 6) it can be assumed that the flow rate prior to ignition decreased because of increased viscosity as well as because of the slower valve opening rate.

(2) Ignition lag alone is not a suitable criterion of the usefulness of a proposed igniter fuel, but is rather an index of the allowable flow rate prior to ignition for a fixed engine configuration.

Thus a material with a long ignition lag, but with other desirable properties, could still be useful as an igniter fuel when low initial flow rates are permissible.

Optimum valve opening time for ignition. - With a fixed quantity of igniter fuel, maximum chamber pressure during ignition was developed for valve opening times greater than the minimum required to obtain ignition. This effect is illustrated by the data of figure 8 for a temperature of -65° F.

It would be anticipated that as valve opening time is decreased, the chamber pressure which developed would increase because of the increased flow rate of propellants; therefore, the decrease in developed pressure with further decrease in valve opening time can be explained by the assumption that the fuel is entering at a faster rate than it can be consumed in the reaction.

Effect of temperature on transition process. - With all the igniter fuels investigated, transition to gasoline could be obtained at 40° F, but could not be obtained at -40° F, as shown in summary in the following table:

Oxidant	Igniter fuel	-85° F		-40° F		40° F	
		Igni-tion	Tran-sition	Igni-tion	Tran-sition	Igni-tion	Tran-sition
WFNA	[a]Hydrazine hydrate	Propellants freeze		Yes	No	Yes	Yes
WFNA	[a]Hydrazine hydrate plus 5 percent suspended gasoline	Propellants freeze		Yes	Yes	Yes	Yes
RFNA	50 Percent triethylamine, 50 percent diallylaniline	Yes	No	Yes	No	Yes	Yes
RFNA	70 Percent triethylamine, 30 percent orthotoluidine	Yes	--	Yes	No	Yes	Yes
RFNA	63 Percent triethylamine, 27 percent orthotoluidine, 10 percent gasoline (MIL-F-5572)	---	--	Yes	No	---	---

[a]64 percent hydrazine

For use with the same thrust cylinder design as was employed in this investigation, Aerojet Engineering Corporation has designed a propellant valve which gives transition from hydrazine hydrate to gasoline at -40° F with white fuming nitric acid (ref. 8). The flow characteristics of this valve are such that a small amount of gasoline enters the chamber along with hydrazine hydrate during the ignition phase.

With the present engine configuration, this condition was simulated by suspending 5 percent gasoline in the hydrazine hydrate, whereupon, as shown in the preceding table, transition was obtained at -40° F. When 10 percent gasoline was dissolved in the triethylamine - orthotoluidine blend, a similar transition at -40° F could not be obtained. Thus it appears that in an engine of low characteristic length it is necessary to introduce the gasoline discretely while a substantial portion of the igniter fuel is still entering the chamber and reacting.

Effect of running-fuel reactivity on transition. - The effect of running-fuel reactivity on transition temperature limits is summarized in the following table:

Increasing chemical reactivity with RFNA	Running fuel	-85° F	-40° F	40° F
↓	Gasoline (MIL-F-5572) Toluene Turpentine	No transition		
	Triethylamine	Transition		

For this study, the igniter fuel was 70 percent triethylamine, 30 percent orthotoluidine and all other factors such as flow program, propellant quantities, and engine geometry were fixed.

As reactivity increases from gasoline to triethylamine, the limiting temperature for transition decreases to -85° F, which is near the melting point of the acid. This scale of reactivity is somewhat arbitrary and is based on the following considerations:

(1) Gasoline reacts sluggishly with nitric acid at room temperature

(2) At room temperature, toluene reacts vigorously with nitric acid to yield oxidation products and nitro compounds

(3) Turpentine ignites with mixed acid (13 percent sulfuric, 87 percent nitric) at -40° F, but not with red fuming nitric acid

(4) Triethylamine ignites with red fuming nitric acid at -40° F

These data indicate that the lower the activation energy of a running fuel and oxidant, the lower will be the permissible starting temperature, provided the materials have suitable physical properties. It would also appear that a precise flow program is a primary factor only with relatively nonreactive fuels such as hydrocarbons.

Tar-forming tendencies of igniter fuels. - At low temperatures many igniter fuels tend to form tar and coke because of incomplete reaction with the acid. This tendency is most troublesome when an ignition failure occurs. In such a case the igniter-chamber orifice or the injector holes, and in the case of a small engine, the exit nozzle, may become blocked by a mixture of tar and coke, thereby increasing the possibility that a repeated attempt to start will result in a malfunction or explosion.

In figure 9 is shown a typical deposit on the injector face for a run in which igniter fuel only was used and ignition took place. The chamber and convergent portion of the nozzle were much more heavily coked than the injector.

In table I is shown how the structure of the igniter fuel influences the coking tendency. Noncarbonaceous fuels, like hydrazine hydrate, produce no deposits. Fuels derived from aliphatic hydrocarbons produce less tar than aromatic fuels; and, in general, as the aromatic content of the fuel increases, the tendency to form tars increases. Dilution of aromatic fuels with triethylamine tends to reduce the absolute amount of tar formed.

CONCLUDING REMARKS

The results obtained in this investigation are so dependent upon engine design and method of flow control that the conclusions should be applied only in a qualitative manner to other engine configurations. Thus, in engines of roughly twice the characteristic length of the one employed in this study, other investigators have obtained satisfactory starts with hydrazine hydrate (69 percent hydrazine) at -40° F even though no gasoline entered with the igniter fluid.

SUMMARY OF RESULTS

The starting of the gasoline - nitric acid system by an igniter fluid, injected ahead of the gasoline, which ignites spontaneously with the acid, was investigated in a 200-pound-thrust engine with a characteristic length of 30 inches. The results of this investigation can be summarized as follows:

1. Blends of diallylaniline or orthotoluidine with triethylamine ignited satisfactorily at -85° F with a red fuming nitric acid containing approximately 19 percent nitrogen dioxide and 3 percent water.

2. As the temperature was decreased, the permissible valve opening time to obtain ignition increased at a rate which roughly paralleled the increase in ignition lag of the igniter fuel.

3. With the transition flow program used, transition to gasoline was possible at 40° F with all igniter fluids tried; whereas at -40° F transition to gasoline was possible only with an igniter fuel which consisted of a 5 percent suspension of gasoline in hydrazine hydrate. An igniter fuel consisting of an orthotoluidine, triethylamine, gasoline blend in which the gasoline is soluble failed to give transition at this temperature.

4. As reactivity of the running fuel was increased by changing from gasoline to toluene to turpentine to triethylamine, the temperature at which transition could be obtained decreased from 40° to -85° F, while maintaining all other factors constant.

5. The tendency of igniter fuels to form tars and coke in the thrust cylinder decreased as the aromatic content of the material was decreased.

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   Bur. Aero., Navy Dept.)

TABLE I - EFFECT OF IGNITER-FUEL COMPOSITION ON AMOUNT OF

RESIDUE DEPOSITED IN COMBUSTION CHAMBER

Chemical classification	Igniter fuel	Chamber condition
Noncarbonaceous	Hydrazine hydrate	Clean
Aliphatic	Mixed alkyl thiophosphites	Clean
	50 Percent diallylamine, 50 percent triethylamine diallyl sulfide	Increasing deposits ↓
Aromatic	70 Percent triethylamine, 30 percent orthotoluidine	
	50 Percent triethylamine, 50 percent diallyl aniline	Heavy deposit

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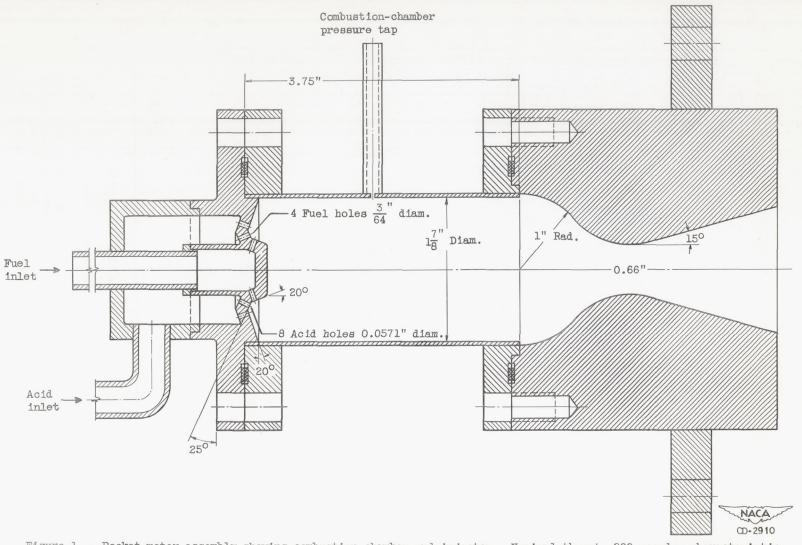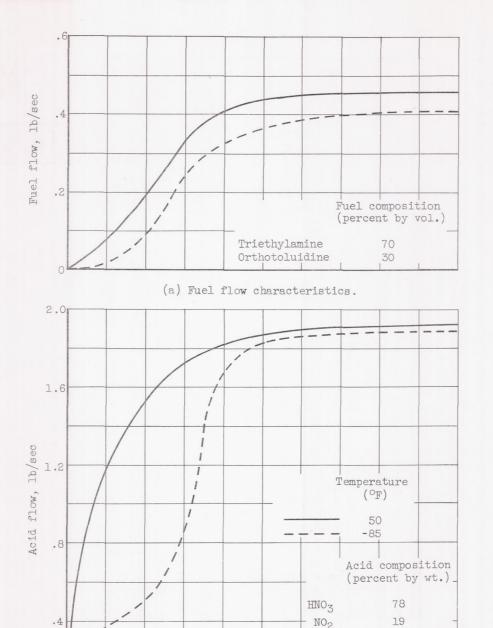
Figure 1. - Rocket motor assembly showing combustion chamber and injector. Nominal thrust, 200 pounds; characteristic length, approximately 30 inches.

(a) Fuel flow characteristics.

(b) Acid flow characteristics.
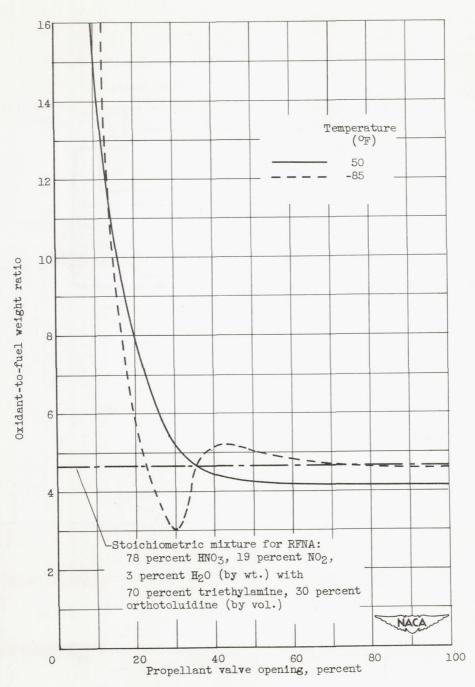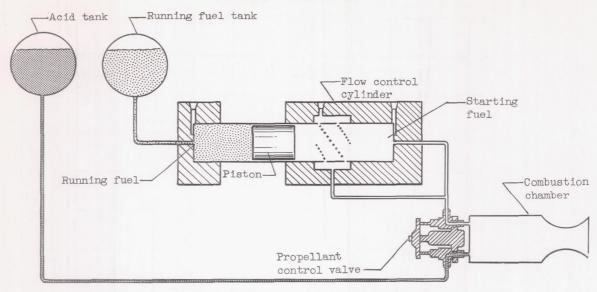
Figure 2. - Calculated propellant flow and mixture ratio as a function of percent valve opening for combination of propellant valve and injector. Propellant supply pressure, 550 pounds per square inch gage; atmospheric pressure in combustion chamber.
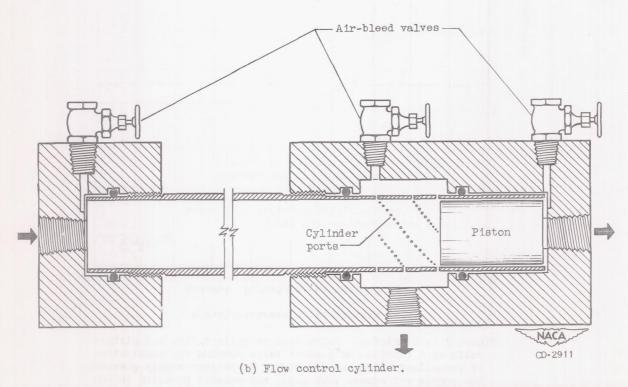
(c) Mixture ratio characteristics.
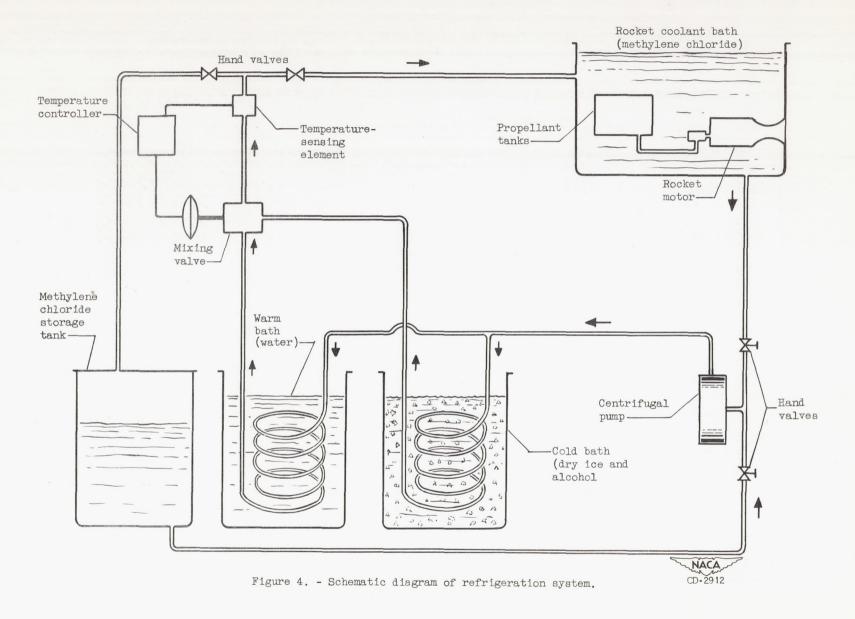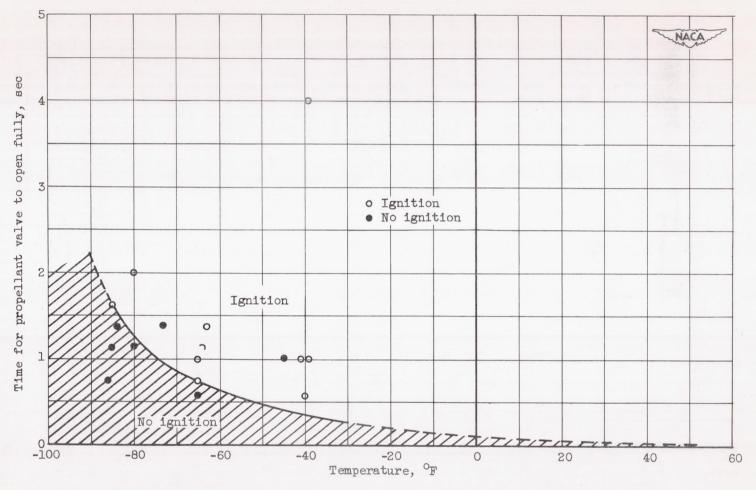
Figure 2. - Concluded. Calculated propellant flow and mixture
ratio as a function of percent valve opening for combination
of propellant valve and injector. Propellant supply pressure,
550 pounds per square inch gage; atmospheric pressure in com-
bustion chamber.

Acid tank — ⌐Running fuel tank

Flow control
cylinder

Starting
fuel

Running fuel — Piston

Combustion
chamber

Propellant
control valve

(a) Rocket motor propellant system.

Air-bleed valves

Cylinder
ports   Piston

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CD-2911

(b) Flow control cylinder.

Figure 3. - Schematic diagram of rocket motor propellant system and flow control cylinder.

Rocket coolant bath
(methylene chloride)

Hand valves

Temperature
controller

Temperature-
sensing
element

Propellant
tanks

Rocket
motor

Methylene
chloride
storage
tank

Mixing
valve

Warm
bath
(water)

Centrifugal
pump

Hand
valves

Cold bath
(dry ice and
alcohol

NACA
CD-2912

Figure 4. - Schematic diagram of refrigeration system.
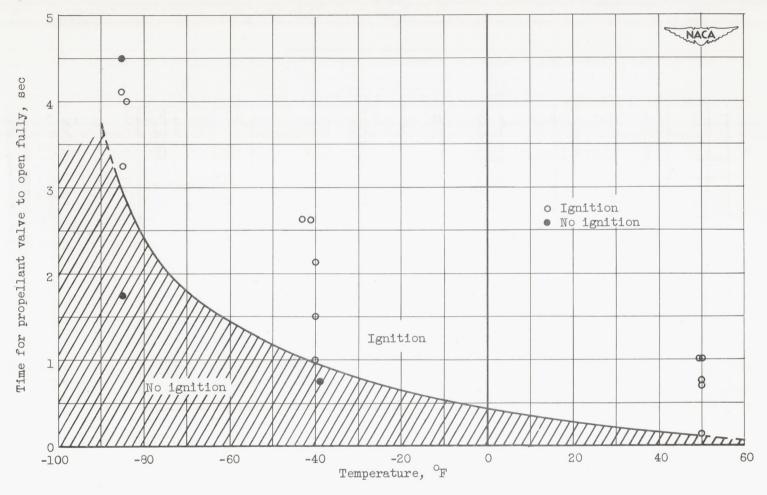
(a) Acid composition: 77.7 percent nitric acid, 18.7 percent nitrogen dioxide, 3.6 percent water (RFNA 1).

Figure 5. - Minimum valve opening time that will permit ignition as a function of initial ambient temperature. Igniter fuel: 70 percent triethylamine, 30 percent orthotoluidine.
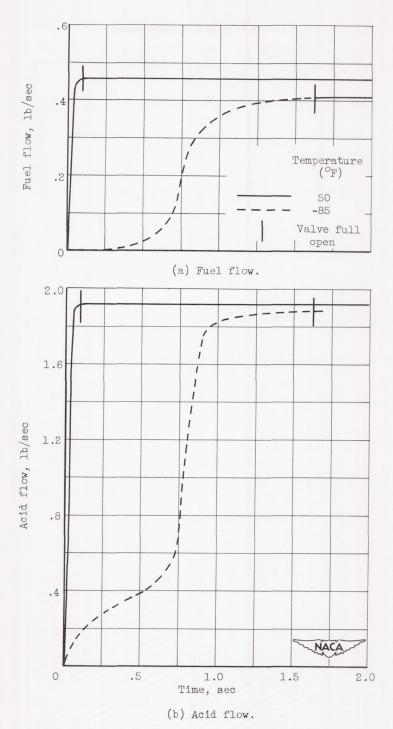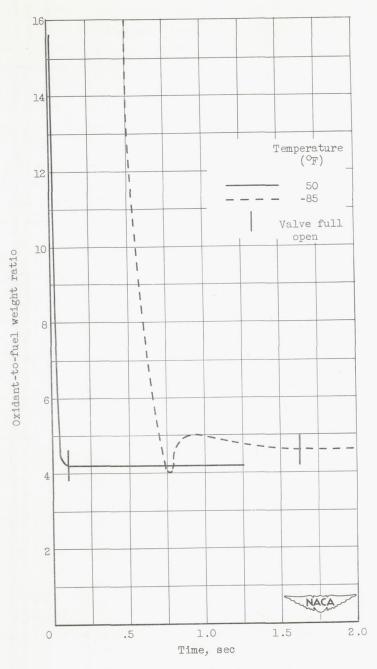
(b) Acid composition: 76.0 percent nitric acid, 18.4 percent nitrogen dioxide, 5.6 percent water.

Figure 5. - Concluded. Minimum valve opening time that will permit ignition as a function of initial ambient temperature. Igniter fuel: 70 percent triethylamine, 30 percent orthotoluidine.

(a) Fuel flow.

(b) Acid flow.

Figure 6. - Comparison of calculated propellant
flow rates and corresponding mixture ratios
that permitted ignition at 50° and -85° F.
Propellants were RFNA 1 (18.7 percent NO_2,
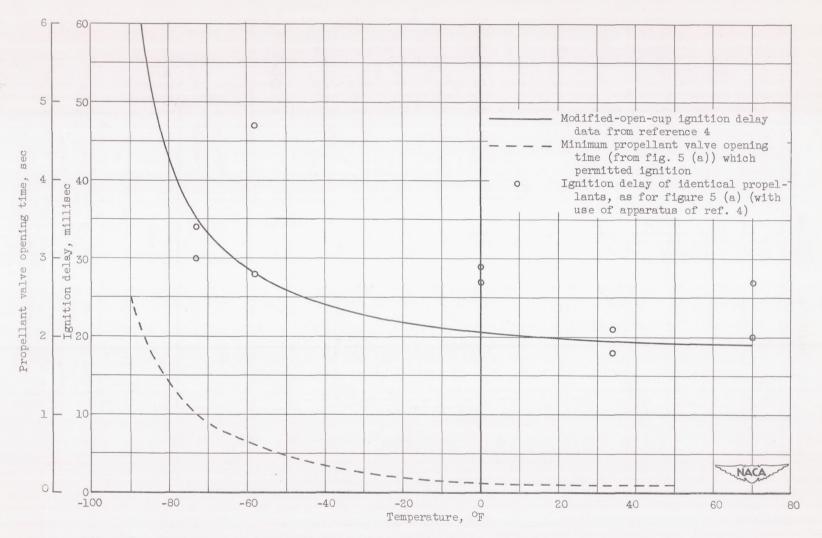3.6 percent H_2O); and 70 percent triethylamine,
30 percent orthotoluidine.

(c) Oxidant-to-fuel weight ratio.

Figure 6. - Concluded. Comparison of calculated
propellant flow rates and corresponding mixture
ratios that permitted ignition at 50° and -85° F.
Propellants were RFNA 1 (18.7 percent NO_2,
3.6 percent H_2O); and 70 percent triethylamine,
30 percent orthotoluidine.

Figure 7. - Comparison of ignition delay with minimum allowable propellant valve opening time for temperature range from -85° to 70° F for propellant system RFNA (70 percent triethylamine, 30 percent orthotoluidine).
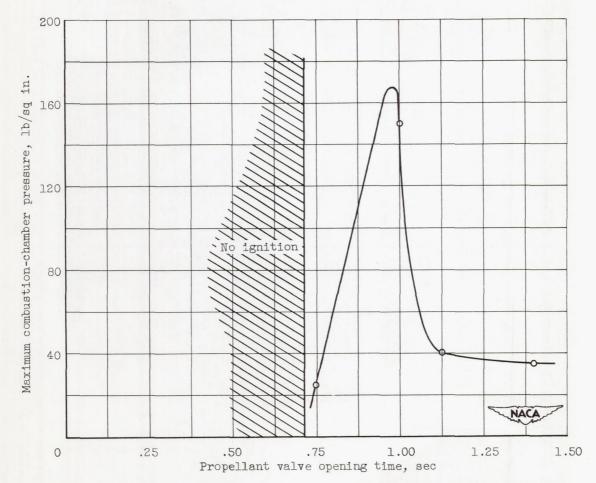
Figure 8. - Effect of propellant valve opening time on maximum combustion-chamber pressure recorded during combustion of 15 cubic inches of 70 percent triethylamine, 30 percent orthotoluidine igniter fuel with RFNA 1. Temperature, -65° F.
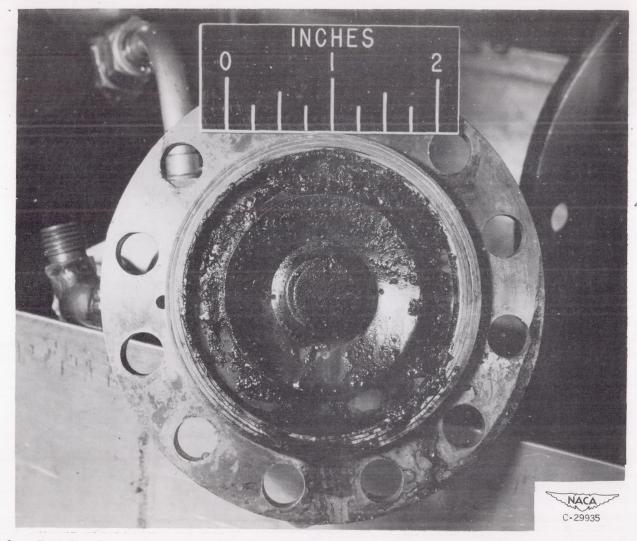
Figure 9. - Example of tar deposit on injector face caused by combustion of igniter fuel when ignition took place.